

Application Report

Cleaning of textiles

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Industry section: Textiles
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Method:



Force Tensiometer – K100



Drop Shape Analysis System
DSA10



Spinning-Drop-Tensiometer
SITE 04

Keywords: Textile cleaning, washing, rewetting, surfactant, cotton, interfacial tension

Assessing the cleaning ability of aqueous surfactant solutions on soiled hydrophobic textile fabrics by using contact angle and surface tension measurements

Low costs – great effects!

Abstract

Wettability and adhesion as well as water- or dirt-repellent properties are determined by surface energy quantities. These play a key role in problems concerning hydrophilicity/hydrophobicity and optimization of the cleaning process. The surface energy of the uppermost monolayers of hydrophobic textile structures can be determined by optical contact angle methods. The suitability of surfactants as cleaning components is usually evaluated by empirical methods, as an explicit evaluation of the cleaning process is difficult from a theoretical viewpoint. The reason is that cleaning processes are very complex and the wetting and rewetting processes on solid surfaces are overlaid by the solubility properties of the soiling agent in the liquid volume phase. This article presents a practical way of making an estimation based on surface tension measurements between dirt components and the cleaning solution as well as on contact angle measurements made on hydrophobic textiles; this makes it possible to predict the cleaning effect.

The basis for the mechanism of many technical washing and cleaning processes, such as soil removal, wetting, dispersing and soil carrying properties, is given by the adsorption of surfactants. As a result of their asymmetrical polar/non-polar molecular construction, surfactants become enriched at boundaries. In an aqueous phase such processes, in which the hydrophobic and not the hydrophilic surfactant component are more or less forced out of the water, are energetically favored. The resultant adsorption depends to a large extent on the class of surfactant and the concentration of the hydrophilic and hydrophobic molecule components. With aqueous solutions the adsorption of surfactants which occurs at the solid/liquid interface of largely nonpolar solids takes place in such a way that the hydrophilic groups of the surfactant molecules contained in the adsorption layer are directed toward the aqueous phase. The adhesion of the surfactant molecules to the solid substrate can usually be explained by van der Waals interactive forces across the hydrophobic molecule component. In this way an originally hydrophobic surface becomes more or less strongly hydrophilized.

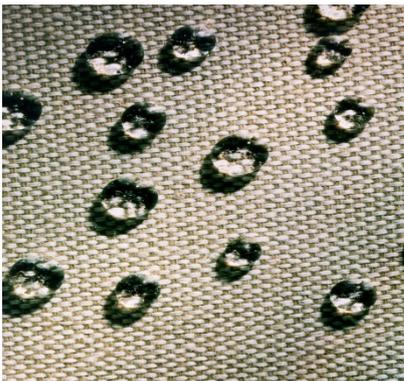


Fig. 1: Drops of water on hydrophobic fabric

The central problem in the evaluation of the cleaning effect on solid surfaces by solutions containing surfactants is the formulation of the Gibbs' enthalpy for rewetting, as under isothermal-isobaric conditions this quantity provides the basic statements about the thermodynamic equilibrium. With the aid of the free wetting enthalpies and the interfacial tension between the oil phase (soiling agent) and aqueous phase (cleaning solution containing surfactants) it is possible to predict the cleaning effect; this is usually understood to be the ratio of the soil-free, i.e. cleaned surface, to the total surface of the solid. The introduced degree of cleanness or rewetting therefore links the possible rewetting, given by the free standard rewetting enthalpy, with the soiled and cleaned surface fractions which are in equilibrium. In order to depict the wetting and rewetting of a solid from the point of view of the interfacial energetic considerations, the cleaning effect of an aqueous solution of a nonionic surfactant (alkylpolyglycoside) on textile fabrics soiled with n-octane has been investigated. In the description of cleaning processes *Koppe, Kling and Lange* have introduced the term rewetting [1], [2].

Rewetting processes can be discussed from both a thermodynamic and a kinetic viewpoint. The kinetic influences include the rewetting kinetics itself, the flow behavior in the washing liquid, the rate of soil binding onto the adsorbents contained in the cleaning agents as well as the transport of these adsorbents to the corresponding interface. In the following observations we have limited ourselves to processes for which the rewetting mechanism is determined purely thermodynamically [3].

Theory

The adhesion of a substance, e.g. a soiling agent containing fat or oil, to a solid surface is determined by interactive forces. With a large number of points of contact, small forces are sufficient to achieve a high degree of adhesion [4]. Such relatively "weak" forces represent the purely disperse van der Waals interactive forces, with which a nonpolar soiling agent is retained on the solid surface [5]. The larger these forces are, the more difficult is the cleaning process and the lower the degree of thermodynamic cleaning. The dewetting or detachment of the soil from the surface can be described by both thermodynamic [6] and hydrodynamic models [7].

Young's equation is used as a basis for deriving a thermodynamic relationship for the rewetting process; in order for it to be valid conditions of thermodynamic equilibrium are assumed:

$$\sigma_{sl} = \sigma_s - \sigma_l \cdot \cos(\theta) \quad (1).$$

σ_l : interfacial tension solid/liquid

σ_s : surface tension of solid

σ_l : surface tension of liquid

θ : contact or wetting angle

The free standard wetting enthalpy is defined by Gibbs as follows [8]:

$$\Delta_{Ben} G^0 = \sigma_{sl} - \sigma_s = -\sigma_l \cdot \cos(\theta) \quad (2).$$

Under the assumption that a soil component I_1 is located on a level, homogeneous solid and that this solid is initially completely covered by it, the rewetting with a liquid (cleaning solution) I_2 can be described according to [3]. As a result a mathematical description for the degree of soiling α_1 , can be obtained; this gives the ratio of the solid surface covered with the soiling agent to the total solid surface:

$$\alpha_1 = a_{s/I_1} / a_{s/I_1}^0 \quad (3).$$

α_1 can have values between 0 (complete rewetting) and 1 (no rewetting). If the soiling agent is oil and a complete spreading of the oil phase on the aqueous phase is assumed then, according to [3], the following relationship applies to the participating surfaces at thermodynamic equilibrium:

$$a_{I_1/I_2}^{eq} = a_{s1/I_1}^{eq} \quad (4).$$

This means that for the degree of residual soiling at equilibrium on a level solid the following mathematical equation can be postulated:

$$\alpha_{1,1,eq} = \sigma_{11/12} / (\sigma_{11/12} + (\Delta_{Ben} G_1^0 - \Delta_{Ben} G_2^0)) \quad (5).$$

Equation 5 represents the basis for the estimation of the degree of residual soiling at equilibrium (or the degree of cleaning at equilibrium) from the quantities interfacial tension and free standard wetting enthalpy, which are easily accessible experimentally (determined from surface tensions and contact angle measurements). The dependency of the free standard wetting enthalpy on the concentration is given by the Gibbs' adsorption isotherm and is discussed in detail in [9] and [10].

Methods and substances

Measurements of the surface tensions of the liquids used were made with a KRÜSS Force Tensiometer – K100 (Fig. 2) using the Wilhelmy plate method.



Fig. 2: KRÜSS Force Tensiometer – K100

The very small interfacial tension of the surfactant/n-octane system used ($< 1 \text{ mN/m}$) was measured with the SITE 04 Spinning Drop Tensiometer (Fig. 3). In this case the approximation according to Princen et al. [11] was used as this allows the interfacial tension to be determined from the diameter of a rotating drop of the lighter phase in the heavier phase under certain limiting conditions.



Fig. 3: KRÜSS Spinning-Drop-Tensiometer SITE 04

Contact angle measurements on the hydrophobic textile surfaces were carried out with the DSA10DO4 Drop Shape Analysis System using the sessile drop method (Fig. 4).



Fig.4: KRÜSS drop shape analysis system DSA10

For the preparation of the cleaning solution a surfactant of the alkylpolyglycoside group (APG 2761, Hüls) was used as the wetting agent and 2-methyl-propanol-(1) as the auxiliary wetting agent.

n-Octane was used for the preparation of a defined model soiling agent on the textile fabric. Scoured, bleached and colored cotton were used as the textile fabrics.

The hydrophobicity of the various cotton fabrics used was evaluated before the start of the investigation by making contact angle measurements with water (Tab. 1). Static contact angle measurements were made with an aqueous surfactant solution at a low initial concentration (Tab. 2). The suitable auxiliary wetting agent was determined by making contact angle measurements with various alcohols. The textile fabrics were intensively wetted with the model soiling agent n-octane. Static contact angle measurements were carried out with aqueous surfactant solutions at various initial surfactant concentrations on the cotton fabrics coated with the model soiling agent in order to optimize the cleaning solution (Fig. 6-9).

The contact angle values obtained with the optimized cleaning solution and the textile fabrics (Tab. 3) together with the free standard wetting enthalpies determined from surface and interfacial tension measurements (Tab. 3) were used to calculate the degree of residual soiling after the use of the optimized cleaning solution for a washing cycle (Tab. 4).

Results

The static contact angle measurements carried out on the textile fabrics with water show that the textile surfaces have a definite hydrophobic property.

Fabric	Contact angle CA (°)
Cotton, scoured	136.1
Cotton, bleached	138.3
Cotton, colored	116.2

Table 1: Static contact angle measurements with water on textile fabrics

As a result of the high hydrophobicity of the textile fabrics it is necessary to be able to achieve a large rewetting effect with a relatively small difference between the wetting potentials. This is why very small interfacial tensions are required between the soiling and cleaning agents. Aqueous solutions of alkylpolyglycosides with the addition of alcohols do have such low interfacial tensions. This is why the alkylpolyglycosides, a somewhat unusual class of surfactants for use in washing processes, are used for evaluating the degree of cleaning (or degree of residual soiling) on hydrophobic cotton fabrics.

Fabric	Contact angle (°)
Cotton, scoured	85.3°
Cotton, bleached	90.1°
Cotton, colored	74.9°

Table 2: Static contact angle measurements with an aqueous surfactant solution (APG 2761, $c_0 = 2.31 \text{ g/l}$) on textile fabrics

In order to select a suitable auxiliary wetting agent for improving the effectiveness of the APG 2761, various alcohols (n-propanol, i-propanol, n-butanol, 2-methyl-propanol-(1) and decanol) were tested by making contact angle measurements. Only tertiary butanol (2-methyl-propanol-(1)) showed the rapid adsorption on the textile fabrics required for a suitable auxiliary wetting agent. All other alcohols tested showed static equilibrium angles on the test fabrics as the results of the contact angle measurements, or had a very slow adsorption rate on the textile structure. This is why 2-methyl-propanol-(1) was selected as the auxiliary wetting agent. Optimization of the volume fraction of tertiary butanol in the aqueous solution was carried out by making contact angle measurements with the binary mixture as a function of the volume concentration of the alcohol. The results of these measurements are shown in Fig. 5.

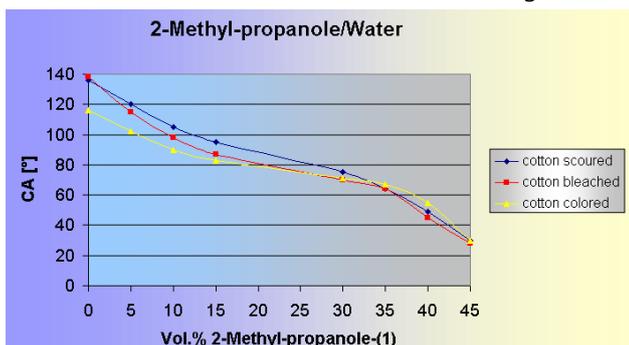


Fig.5: static contact angle measurement with a binary blend 2-methyl-propanol-(1)/water in dependence on the volume breach

The results of the contact angle measurements carried out for the optimization of the cleaning solution as a function of the initial surfactant concentration and the concentration of the wetting agent are shown in Figures 6 to 12.

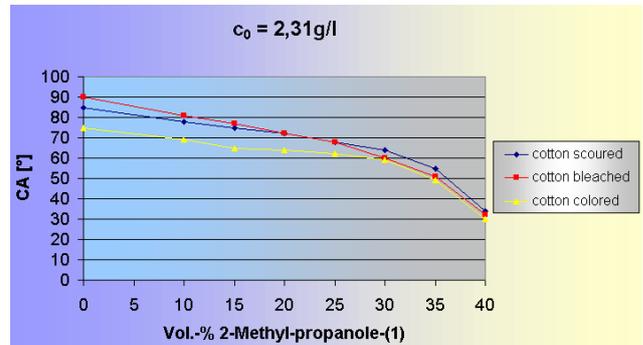


Fig.6: static contact angle measurement in dependence on the volume percent of the wetting liquid with an output concentration $c_0 = 2,31 \text{ g/l}$ of the surfactant APG 2761

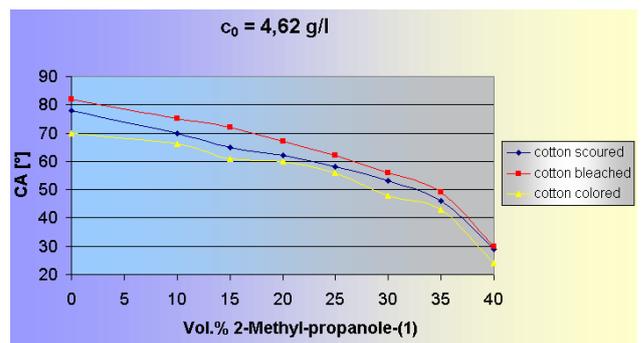


Fig.7: static contact angle measurement in dependence on the volume percent of the wetting liquid with an output concentration $c_0 = 4,62 \text{ g/l}$ of the surfactant APG 2761

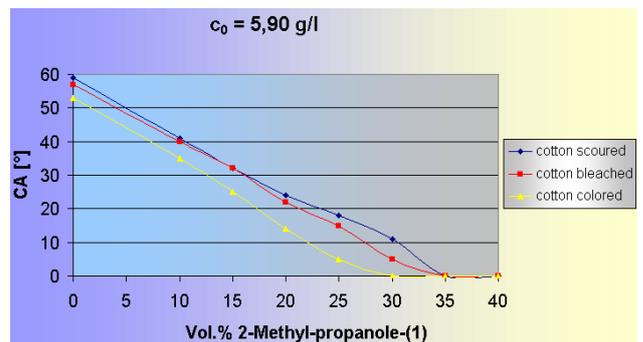


Fig. 8: static contact angle measurement in dependence on the volume percent of the wetting liquid with an output concentration $c_0 = 5,90 \text{ g/l}$ of the surfactant APG 2761

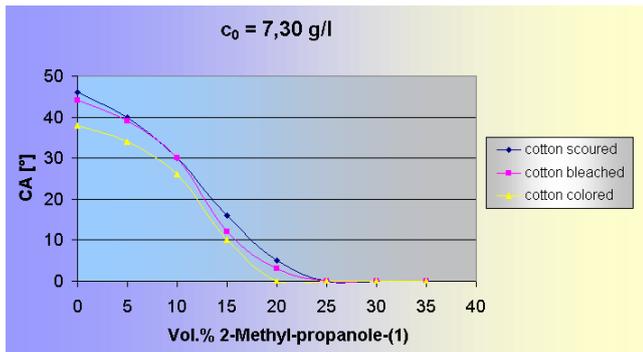


Fig. 9: static contact angle measurement in dependence on the volume percent of the wetting liquid with an output concentration $c_o = 7,30$ g/l of the surfactant APG 2761

From these illustrations it can be seen that the contact angles sink dramatically as the surfactant and alcohol concentrations increase. It was also observed that the wetting rate depended on the size of the equilibrium contact angle. For contact angles $< 90^\circ$ the wetting rate increases as the contact angle decreases. In this case the wetting rate is defined as being the time required for the formation of an equilibrium drop on the fabric. These wetting rates were very small for all three textile fabrics tested (< 30 s), so that a great influence of the washing mechanism on the degree of residual soiling could be expected.

For evaluation of the wetting or dewetting of oil as a model soiling agent we postulate 20° as the upper limit for the contact angle. Theoretically rewetting is also possible at $> 20^\circ$; however, this would require a considerably increased duration for the washing process which, for energy consumption reasons, would be unacceptable. From Figures 10 to 12 it can be seen that, at concentrations up to 10% V/V 2-methyl-propanol-(1), this is not necessary. However, a further increase of the surfactant concentration in the washing solution (> 6.6 g/l) can be discounted for economic reasons. The surface tension of the optimal cleaning solution for removing the model soiling agent (15% V/V 2-methyl-propanol-(1) + 85% V/V aqueous surfactant solution APG 2761 with $c_o = 7.30$ g/l) was determined to be 25.26 mN/m by the Wilhelmy plate method.

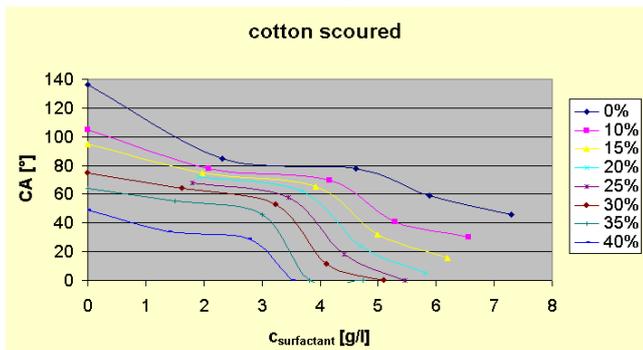


Fig. 10: static contact angle measurement in dependence on the output concentration of the surfactant and the volume percent of the wetting liquid at scoured cotton

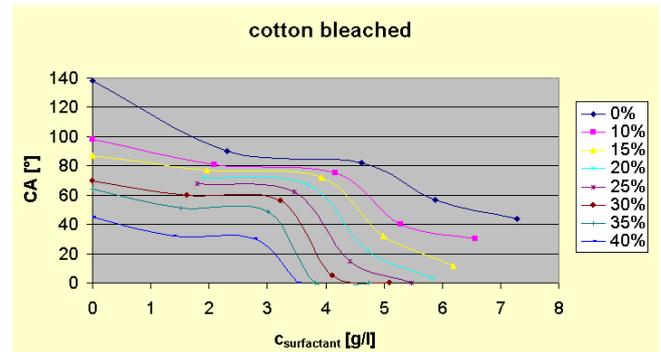


Fig. 11: static contact angle measurement in dependence on the output concentration of the surfactant and the volume percent of the wetting liquid at bleached cotton

At this surfactant concentration (see Fig. 9) the contact angle measurements gave the values for the free standard wetting enthalpy $\Delta_{Ben}G^0 = -\sigma_1 \cos(\theta)$ shown in Tab. 3.

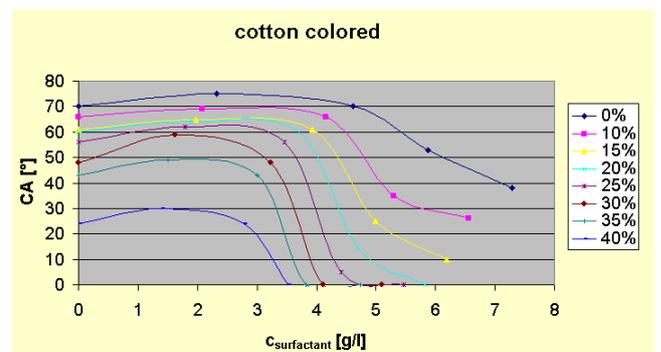


Fig.12: static contact angle measurement in dependence on the output concentration of the surfactant and the volume percent of the wetting liquid at colored cotton

Fabric	Contact angle CA (°)	Free standard wetting enthalpy $\Delta_{Ben}G^0$ (mJ/m ²)
Cotton, scoured	16.8	-24.18
Cotton, bleached	13.5	-24.56
Cotton, colored	11.5	-24.75

Table 3: Contact angles and free standard wetting enthalpies for textile fabrics with optimized cleaning solution (15% V/V 2-methyl-propanol-(1) + 85% V/V aqueous surfactant solution APG 2761, $c_o = 7.30$ g/l)

The surface tension of n-octane was determined to be 20.87 mN/m. The interfacial tension between the model soiling agent n-octane and the optimized cleaning solution was determined to be 0.32 mN/m. For optimal wetting between the model soiling agent n-octane and the textile fabric as a precondition for heavy soiling a contact angle of 0° is assumed. Provided that the contact angle between n-octane and the textile surface remains $> 0^\circ$, this would indicate a poorer wetting between the model soiling agent and the solid surface which ought to be the starting point for an improved cleaning result.

This cleaning result is in the form of the calculated degrees of residual soiling at equilibrium α , which have been calculated for a simple washing process from the experimentally determined values for the surface tension of n-octane, the free standard wetting enthalpy of the optimized cleaning solution on the textile fabrics and the interfacial tension between n-octane and cleaning solution, and are shown in Table 4.

Fabric	Degree of residual soiling at equilibrium α (%)
Cotton, scoured	8.9
Cotton, bleached	8.0
Cotton, colored	7.6

Table 4: Degree of residual soiling at equilibrium of textile fabrics after wetting with optimized cleaning solution (15% V/V 2-methyl-propanol-(1) + 85% V/V aqueous surfactant solution APG 2761, $c_o = 7.30$ g/l)

Carrying out the washing cycle several times increases the degree of cleaning. A degree of residual soiling < 1% can be achieved for the investigated cotton fabrics after only two washing cycles. As the high concentrations of both the surfactant and alcohol in the cleaning solution are unacceptable for economic reasons, the effect of pretreating the textile fabrics before the washing process itself is carried out should be investigated. This could be done by first spraying the fabric to be cleaned. A detailed presentation and evaluation of this process in combination with the subsequent washing process and the choice of different washing solutions will be the subject of one of the next Application Reports.

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